

TITLE: REDUCTION OF INHERENT MERCURY
EMISSIONS IN PC COMBUSTION

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I. ABSTRACT

OBJECTIVE: At present, mercury emission compliance presents one of the major potential challenges to the electric utility industry raised by the Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in retention of mercury by ash in field data suggests that means exist to reduce inherent mercury emissions, if the factors controlling the variability can be identified and controlled. Key steps appear to include the oxidation of elemental mercury to Hg^{++} , generally producing the more reactive and water soluble HgCl_2 . Some forms of oxidized mercury appear to have a capacity to form complexes with certain types of fly ash aerosols. The principal thrust of the research focuses on identifying the rate-limiting steps associated with high-temperature mercury oxidation via HCl and other chlorine species derived from HCl.

WORK DONE AND CONCLUSIONS: The entrained flow coal reactor was modified to provide a near isothermal environment with $T=200\text{-}1300^\circ\text{C}$ and one second residence time. An air-assist atomizer was added into the flame zone to atomize a dilute mercuric acetate solution into the flame. The high temperature of the flame provides for vaporization of the mercury and reduction into Hg^0 . A sonic air staging lance partway through the furnace adds sufficient dilution air to reduce the furnace gas temperature to the target level. Hydrochloric acid is added to the furnace gases along with this dilution air. The relatively low surface/volume ratio of the furnace is designed to prevent surface reactions, particularly the reduction of oxidized mercury noted on convective surfaces at lower temperatures. For this reason, dilution cooling of the flame gases to the target temperatures was preferred over the use of high surface area convective cooling.

A modified version of the Method 29 multimetals train is used for analysis. This method was determined to be adequate for oxidation-state speciation since neither of the interfering species Cl_2 or SO_2 are present in the experiment. Mercury is determined by cold vapor atomic absorption after it is released from the digested catch solution by reduction.

Testing has examined the factors controlling gas-phase mercury oxidation. We have built an extensive database on the extent of oxidation as a function of both temperature and HCl under pulverized coal conditions. This gives us a direct comparison with the much more complete MSW database in the literature. (The MSW data are characterized by much higher mercury and HCl concentrations than are typical in pulverized coal combustion.) As discussed below, the data suggest a controlling free radical mechanism for high-temperature oxidation. This is presently being examined by a test series that focuses on the manipulation of the free radical population in a known way to determine if mercury

oxidation responds in a way that is consistent with the hypothesis. The vehicle for manipulating the free radical populations is the use of trace amounts of H_2 and CO in the HCl injection stream. We are continuing these tests which focus on the role of free radicals as promoters of the oxidation process.

Some tentative results suggest a direct role of certain metals catalyzing the reduction of oxidized Hg under at low temperatures. This is to be explored following the homogeneous testing.

A kinetic model of the high-temperature oxidation process involving elementary reactions has been assembled and tested. The model makes use of a literature mechanism for the behavior of the HCl/Cl/Cl₂ system to establish the population of Cl-atoms and Cl₂ as a function of temperature. A literature value of the rate constant for the second-order reaction of Cl-atoms with Hg⁰ is used ($Hg + Cl = HgCl$, $HgCl + HCl = HgCl_2 + H$). A competing pathway for oxidation by Cl₂ based on rates derived from the data of Hall et al. is also included. The resulting behavior closely replicates the experimental data generated in this program. The results suggest that the reaction is exclusively via Cl-atom oxidation at high temperature, with the Cl₂ concentrations being about two orders of magnitude too low to participate in the oxidation. This explains the anomaly in the Hall data in which conversion to Hg⁺⁺ increases at the highest temperatures examined, in contradiction of the trends predicted by equilibrium analysis. The need for Cl-atoms as a driving force indicates that the reaction will only be favored at higher temperatures where chlorine atom concentrations are significant.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The results of DOE- and EPRI-sponsored field testing show that organic emissions are generally insignificant. Likewise, most toxic metals are collected to greater than 90% concentrations in modern particulate control devices. The principal exceptions are Hg, Se, U-238, and Pb-210. The mercury and selenium are the least well controlled, with the Hg presenting the greatest environmental risk. Thus, Hg presents one of the greater possible challenges to coal-based power production arising out of the Clean Air Act Amendments. While Hg is well-controlled in spray dryer systems using activated carbon additives, not all sources are equipped with this equipment. The variability noted in the field data suggests that mechanisms promoting Hg retention onto fly ash exist. The current project is directed towards identifying the steps that control this process and suggesting means of promoting retention in full-scale systems without undue cost or system modification.

PLANS FOR THE COMING YEAR:

- Complete free radical oxidation testing.
- Perform a limited matrix examining low-temperature reduction catalytic effects.
- Interpret data with existing kinetic model.

II. HIGHLIGHT ACCOMPLISHMENTS

- Furnace modified to provide an isothermal time/temperature environment with a low surface/volume ratio to prevent catalytic reactions.
- Modified Method 29 Multimetals train set up and tested.
- Elementary studies on Hg oxidation as a function of basic parameters completed.
- Free radical-promoted oxidation of Hg investigated.
- Kinetic free-radical model developed that replicates literature trends.

ARTICLES, PRESENTATIONS, AND STUDENTS

Articles and Presentations

Kramlich, J. C.: Mercury Oxidation in Furnaces: Promotion, Pathways, and Opportunities. Invited presentation to the ACERC Annual Meeting, Provo, Utah (March 1998).

Sliger, R. N., D. J. Going, and J. C. Kramlich: High-Temperature Mercury Oxidation Kinetics. Western States Section/The Combustion Institute, Fall 1998 Meeting, Seattle, Washington, submitted (October 1998).

Going, D. J.: Identification of Rate-Limiting Reactions Associated with HgCl_2 Formation. MS Thesis, Department of Mechanical Engineering, University of Washington, Seattle, Washington (1998).

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